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BRANCHED GLYCIDYL AZIDE COPOLYMERS

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DREV Task Number: 14/1-1991

Scientific Authority of DREV: Dr. E. Ahad

SANS CLASSIFICATION

P154752.PDF [Page: 4 of 42]

105-01850/

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FINAL REPORT
OCTOBER 1995

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ABSTRACT

Second generation branched Glycidyl Azide Polymer (GAP) and branched Glycidyl Azide-Ethylene Oxide Copolymer (GEC) are synthesized at 120°C according to the degradation process developed at DREV using polyepichlorohydrin (PECH) and polyepichlorohydrin-ethylene oxide copolymer (PEEC), respectively, as starting materials, under exactly the same experimental conditions. The main reaction parameters to be varied are: the type of polyol; either glycerol (GOL), trimethyol propane (TMP) or pentaerythritol (PE), as well as its proportion; the cleaving agent concentration; the reaction time and temperature. The average molecular weights (MW) of branched GAP and GEC are measured by the Gel Permeation Chromatography (GPC) and viscometry techniques. In general, GEC has MW values slightly higher than the corresponding branched GAP. Both products are then cured with isophorone diisocyanate (IPDI) at different values of the NCO/OH ratio. The obtained energetic polyurethanes are characterized using Scanning Electron Microscopy (SEM), Thermomechanical Analysis (TMA) and tensile tests. It is found that GEC yielded polyurethane products having higher elongations at break but lower tensile strengths than their branched GAP counterparts.

RESUME

Un poly azoture de glycidyle (GAP) ramifié de seconde génération et un copolymère GAP-oxyde d'éthylène ramifié (GEC) sont synthétisés à 120°C selon le procédé de dégradation développé au CRDV en utilisant le polyepichlorohydrin (PECH) et un copolymère d'epichlorohydrine-oxyde d'éthylène (PEEC), respectivement, comme réactifs principaux, sous exactement les mêmes conditions expérimentales. Les principaux paramètres à être variés sont: le type de polyol; soit glycérol (GOL), triméthylol propane (TMP) ou pentaerythritol (PE), ainsi que leur proportion; la concentration de l'agent de clivage; la température et le temps de réaction. Les GAP ramifiés et copolymères sont caractérisés par les techniques de chromatographie par gel perméable (GPC) et viscométrie pour déterminer leurs masses moléculaires (MM) moyennes. En général, les GEC ont des valeurs de MM sensiblement plus élevées que celles des GAP ramifiés correspondants. Tous ces produits sont ensuite polymérisés avec l'isophorone diisocyanate (IPDI) à différentes valeurs du rapport NCO/OH. Les polyuréthanes énergétiques obtenus sont ensuite caractérisés par les techniques de microscopie électronique (SEM), analyse thermomécanique (TMA), et essais de tension. Les polyuréthanes à base de GEC ont des meilleures élongations à la brisure mais des plus faibles forces de tension que ceux provenant du GAP ramifié.

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EXECUTIVE SUMMARY

Recently, energetic binders have been synthesized for use in high-performance, insensitive, low-smoke rocket propellants. One such energetic binder which could appear in future rocket propellants and plastic bonded explosives is Glycidyl Azide Polymer (GAP) which will be incorporated into new energetic formulations to replace the inert and currently used hydroxyl-terminated polybutadiene binder. GAP was considered as an attractive substitute for inert conventional binders because of its interesting properties and also because it was the first commercially available energetic binder prepared on a relatively large scale. GAP with a linear structure is currently produced in the USA by a two-step process; this linear GAP has a specific molecular weight (MW) of ~ 2000, a hydroxy functionality below 2 and is relatively expensive.

In 1987, a degradation process was discovered at DREV for the preparation in a single step of a first generation Canadian branched GAP by reacting a polyepichlorohydrin (PECH) rubber with epichlorohydrin (ECH) monomer and sodium azide. Recently, an improved process has been developed and patented by DREV for the preparation of second generation branched GAP or Branched Glycidyl Azide-Ethylene Oxide Copolymer (GEC) in one step, without the addition of an epoxide monomer such as ECH. The chemical reaction has been simplified in this novel process which involves both the degradation and azidation of a cheap commercial rubbery PECH or polyepichlorohydrin-ethylene oxide copolymer (PEEC) with sodium azide in the presence of a base (optional) and a polyol (optional) for a few hours at elevated temperatures.

The purpose of this research task is to prepare and characterize some samples of second generation branched GAP and GEC copolymers according to the DREV degradation process by varying some reaction parameters. As the second part of this project, the branched GAP and GEC samples are then cured with isophorone diisocyanate (IPDI) to assess and compare the mechanical properties of the polyurethane products resulting from these polymers.

NOMENCLATURE

CH_3OLi	lithium methoxide
DCM	dichloromethane
DMSO	dimethyl sulfoxide
ECH	epichlorohydrin
GAP	glycidyl azide polymer
GEC	(glycidyl azide - ethylene oxide) copolymer
GOL	glycerol
GPC	gel permeation chromatography
M_{GAP}, M_{PS}	molecular weight of GAP and polystyrene, respectively
M_n, M_w, M_v	number, weight and viscosity average molecular weight, respectively
MW	molecular weight
NaN_3	sodium azide
NaOH	sodium hydroxide
NMR	nuclear magnetic resonance
PE	penthaerythritol
PECH	polyepichlorohydrin
PEEC	polyepichlorohydrin-ethylene oxide copolymer
PS	polystyrene
SEM	scanning electron microscopy
T	asbolute temperature
T_g	glass transition temperature
THF	tetrahydrofuran
TMA	thermomechanical analysis
TMP	trimethylol propane
$[\eta]$	intrinsic viscosity
σ_u	tensile strength
ξ_b	Elongation at break

INTRODUCTION

Glycidyl Azide Polymer (GAP) is a hydroxy-terminated aliphatic polyether containing alkyl azide groups which could be used as an energetic binder in low-smoke solid rocket propellants, composite explosives, gun propellants and pyrotechnics to enhance the performance and stability, reduce the vulnerability and improve the physicochemical properties of the energetic formulations.

GAP with molecular weight (MW 1000 - 6000) is currently produced in the USA (Refs. 1-5) according to a two-step process which requires two distinct reactions (polymerization and azidation). GAP of low MW (approx. 500), which could be used mainly as an energetic plasticizer, can be prepared through a single-step process (Refs. 6-9) developed at DREV.

Branched GAP (first generation) with variable MW (500 - 40,000) can also be prepared directly through a degradation process developed at DREV (Refs. 10-16) by reacting a high MW rubbery polyepichlorohydrin (PECH) with the epichlorohydrin monomer (ECH) and NaN_3.

Recently, a novel degradation process was developed at DREV (Refs. 17-21) for the preparation of second generation branched GAP or Glycidyl Azide-Ethylene Oxide Copolymer with controlled and variable MW (1000 - 200,000), but without using any epoxide monomer such as ECH in the reaction. This process involves the single-step reaction of a high MW solid rubbery PECH or polyepichlorohydrin-ethylene oxide copolymer (PEEC) with NaN_3 in the presence of a basic cleaving agent and a polyol in a suitable solvent at elevated temperature (the cleaving agent and/or the polyol are optional). The MW, viscosity, equivalent weight and hydroxyl functionality of the branched GAP and Copolymer products can be controlled and predetermined by varying the concentration of the reactants.

Linear or branched GAP when used as an energetic binder should be transformed into a long chain polyurethane after the curing reaction using a suitable isocyanate compound such as Hexamethylene diisocyanate (HDI), Diphenylmethane diisocyanate (MDI), Tolylene diisocyanate (TDI), Desmodur N-100 which is a triisocyanate based on HDI. For a given GAP sample, the various isocyanates used should yield polyurethane (PU) products with different mechanical properties, namely the elongation at break and the tensile strength. Usually, these two properties vary inversely, for instance, an aliphatic diisocyanate such as HDI gives rise to PU with a lower tensile strength but a higher elongation at break than the one produced from a diisocyanate containing an aromatic ring such as TDI or MDI (Refs. 14, 15). Recently, another isocyanate compound called Isophorone diisocyanate (IPDI) was used for the curing of branched GAP and this isocyanate compound seemed to yield PU products with a better mechanical performance than the other cited isocyanate compounds (Ref.16).

While branched GAP of the first generation gives rise to PU products with a tensile strength and an elongation at break significantly better than those obtained from linear GAP (Ref. 15), it is desired that the elongation at break of the energetic polyurethanes be further improved in order to

satisfy all mechanical requirements when second generation branched GAP or GAP Copolymers are used as binders in rocket propellant formulations.

The purpose of the present research task is two-fold: first, synthesize second generation branched GAP by following the improved degradation process and then perform curing and testing of the obtained PU products; secondly, replace the starting material PECH in the reaction by a polyepichlorohydrin-ethylene oxide copolymer (PEEC) to produce a branched Glycidyl Azide-Ethylene Oxide Copolymer named *branched GEC*, and then perform characterization of this copolymer as well as carry out the mechanical testing of the cured PU products obtained from this new copolymer. There are the effects of some main reaction parameters to be investigated such as the ratios of polyol/PECH and cleaving-agent/PECH, the temperature, and the reaction time. Comparison between branched GAP and branched GEC will be highlighted.

2.0 SECOND GENERATION BRANCHED GAP

2.1 The Improved Degradation Process

Second generation branched GAP is obtained according to an improved degradation process developed at DREV (Refs 17-21) which does not require the use of ECH in the reaction. Branched GAP with predetermined and variable MW (1000 - 200,000) is prepared in a single step by the reaction of a very high MW rubbery PECH in NaN_3 in the presence of a basic cleaving agent and a polyol in a polar organic solvent at elevated temperature. However, in this process the polyol and/or the basic cleaving agent are optional. The basic cleaving agent is mainly used to control and further reduce the MW of the branched GAP product. The use of a cleaving agent increases the degradation rate and thus make possible the MW reduction in a more extensive manner. The MW of the product can be adjusted to the desired value by varying the cleaving agent concentration in the reaction mixture. The reaction mechanism is well detailed in Reference 20.

The starting PECH reactant mainly used to produce the new branched GAP is a relatively cheap commercial solid rubber (Hydrin 100) manufactured by B.F. Goodrich with a weight average molecular weight (M_w) of 2.8×10^6 and a number average molecular weight (M_n) of 320,000.

2.2 Synthesis of Branched GAP

The solvent used in this synthesis must dissolve the rubbery PECH, sodium azide, the cleaving agent and the polyol, in order to achieve both the degradation and azidation reactions. The suitable solvent chosen is dimethyl sulfoxide (DMSO) which has a very high boiling temperature (189°C).

The rubbery PECH (20 g) is cut into small pieces and dissolved in DMSO (200 g) at 60°C overnight (approx. 15 hs), using a polymerization vessel with four openings: one for the mechanical stirrer, one for the thermometer, the third one for the reflux system and the last opening for the additions of different reactants. The following morning, the temperature is raised to 120°C and agitation is started. Glycerol (GOL) (20 g) is added to the PECH solution and 45 minutes later NaN_3 (16 g) is poured into the mixture. After about 30 minutes the cleaving agent, lithium methoxide (CH_3OLi)(0.6 g) is finally added to the system which is allowed to react for about 7 h. During this time no gelling is observed in the mixture. The system is cooled down overnight in a fridge to allow the salts to crystallize.

2.3 Purification Method

When the synthesis reaction is complete, the final solution is composed of branched GAP dissolved in DMSO, the polyol used, excess azide salt and NaCl. Most of the last two compounds are in fine solid state which can be easily removed from the solution by filtration. It is now necessary to separate the branched GAP from DMSO. Since the branched GAP is supposed to be a non-volatile viscous liquid, a vacuum distillation process, at about 1 mmHg and 80°C, was first attempted to remove DMSO from branched GAP. However, this process is extremely time-consuming due to the very low volatility of DMSO. The liquid extraction method was therefore selected to remove the DMSO.

The first step in the extraction method is to add 400mL of dichloromethane (DCM) to the 200mL of the branched GAP solution (free of solid) to create a less polar organic phase comprised of branched GAP, DMSO and DCM. Secondly, 1200 ml of an aqueous phase formed by methanol-brine (50/50 in weight) is added to the organic phase. The presence of NaCl salt in the aqueous phase helps to reduce the foaming at the interface of the two phases. The whole system is shaken well during which DMSO, due to its strong polar character, is extracted by the aqueous phase. The whole system is then allowed to rest for about 1 hour and separate into two distinct phases where the organic one with its higher density of about 1.32 is at the bottom of the separator flask. There is also a small amount of DCM, as well as oligomers of branched GAP, that goes into the aqueous phase which makes it slightly yellow in colour. The organic phase is now separated by decantation. The extraction process is repeated on this organic phase three more times using the same amounts of aqueous solution. For the last extraction, the system was left overnight to allow the two phases to completely separate. The resulting organic phase was dried using $MgSO_4$ powder. Finally, dichloromethane was evaporated using a rotary evaporator and the final product obtained was the purified branched GAP.

The extraction method for removing DMSO from branched GAP is very efficient, the yield is higher than 90% based on the total amount of PECH used for the branched GAP synthesis. The 10% lost is mainly attributed to the branched GAP oligomers which have passed to the aqueous washing solutions leading to a yellowish colour of the latter. This is advantageous for the extraction method since the obtained product should be more homogeneous with respect to its MW distribution. The extraction method requires several steps that are easy to perform. Each extraction takes approximately one hour, except the last one that is left overnight to allow the two phases to completely separate. These two phases separate easily because of the large difference in their density. The quantities of liquid solutions used for the extraction are optimal. It may be possible to reduce these amounts slightly. The results of extraction may be better if a mechanical agitator is used for a longer period of time in order to effect a better interphase mass transfer of DMSO between the organic and aqueous phases.

2.4 Residual DMSO Concentration measured by NMR Spectra

In order to determine the DMSO concentration remaining in branched GAP samples after each extraction step, a NMR spectrum of the resulting organic phase was taken using a Varian NMR spectrometer, model Gemini 200 MHertz. A spectrum was also taken for the original unextracted solution which is presented by Figure 1. It is found that the peaks attributed to branched GAP are localized between 3 and 4 ppm, the peak of DMSO is at 2.62 ppm, while dichloromethane peak is at 5.3 ppm and finally the one at 7.27 ppm is due to chloroform which is the solvent used for NMR analysis. The spectral region of interest is limited between 2 and 4 ppm because this allows the observation of variations in DMSO and branched GAP concentrations, respectively, after different extraction steps. These variations through the first, second, third and fourth extractions are illustrated by Figure 2. After each extraction step, the relative concentration of branched GAP increased while that of DMSO correspondingly diminished . Table 1 summarizes the peak integration values for DMSO and branched GAP, respectively, after each extraction, as well as the weight percentage of residual DMSO in the branched GAP sample. Details of the calculations for this weight percentage will be discussed later. It is found that after the fourth extraction, there is only about 1% DMSO left in the branched GAP sample. It is also noticed that after the first and the second extractions, most of DMSO was already removed and only 4.4% DMSO is left in the solution. The values of DMSO % in Table 1 are independent of the volume of dichloromethane (DCM) present in the solution. A proof of this observation is that after the DCM was completely evaporated, the NMR spectrum taken on this dried sample also revealed the same DMSO concentration as that shown in Table 1 (i.e. 1%). This spectrum is illustrated by Figure 3 which shows only the peaks of chloroform (solvent used for NMR spectra) and of branched GAP since both DCM and DMSO have been effectively extracted.

Table 1
Effect of Extractions on Residual DMSO Concentration in the GAP Product

Step	Peak Integra. (DMSO)	Peak Integra. (GAP)	%in Weight (DMSO)
Initial	157	22.8	82
1st	132	128	40
2nd	5.23	74.2	4.4
3rd	3.80	100	2.4
4th	2.03	131	1.0
GAP	5.1	313	1.0

Figure 1: NMR Spectrum of the original Unextracted GAP Solution

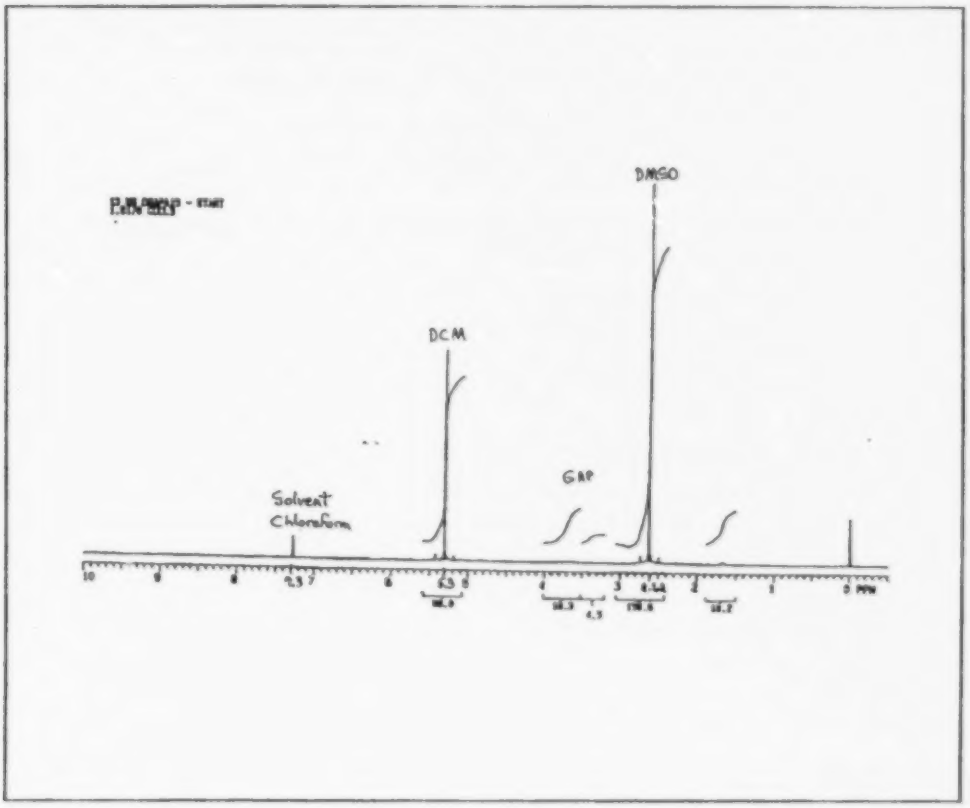


Figure 2: NMR Spectra of GAP Solution after 1st, 2nd, 3rd and 4th Extraction

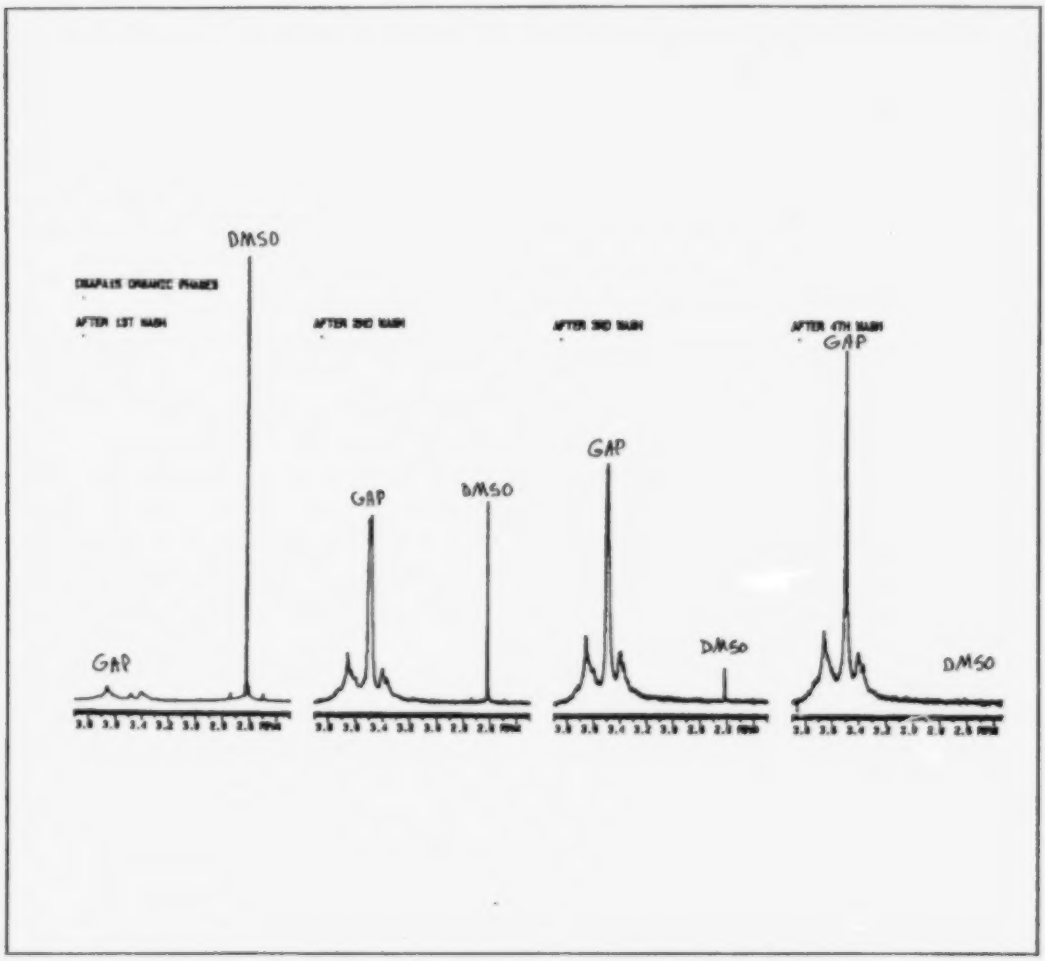
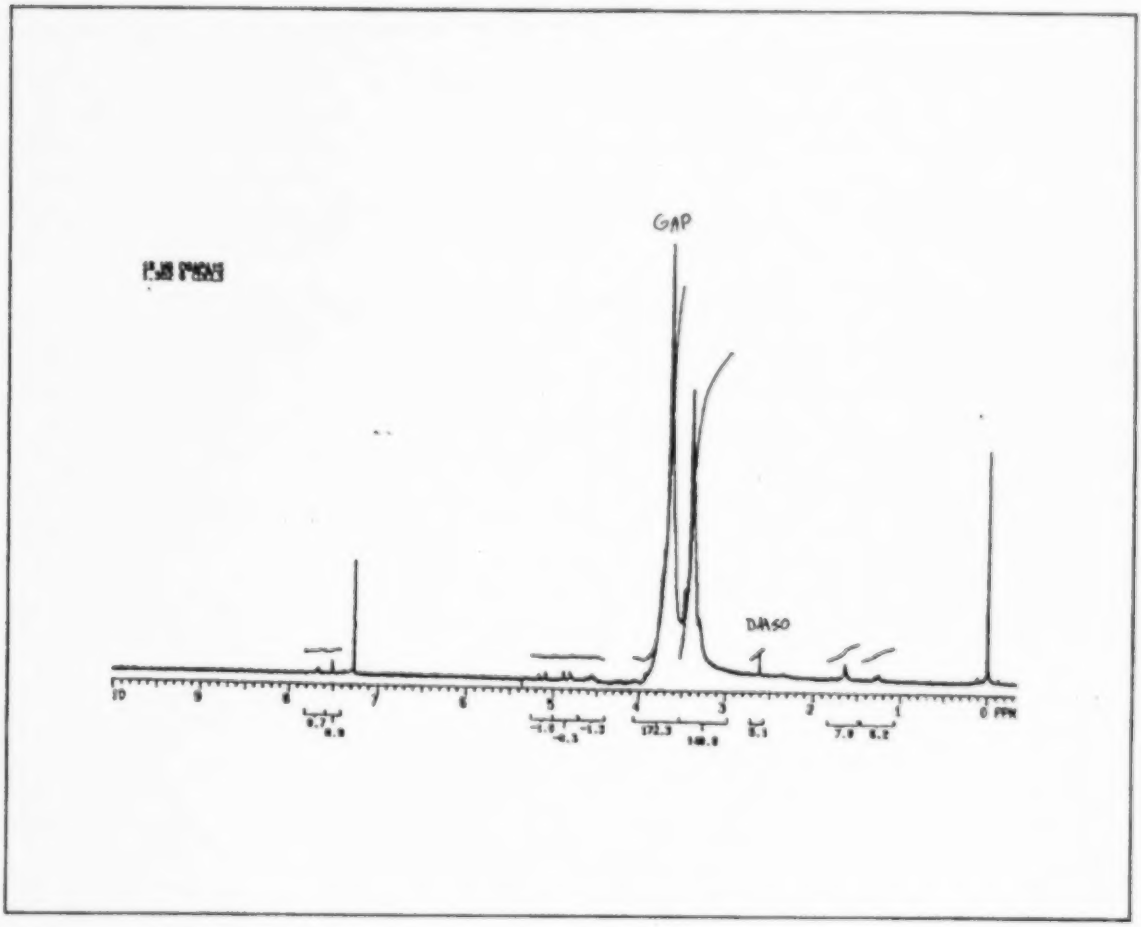


Figure 3: NMR Spectrum of PurifiedGAP Sample



2.5 Proposed method for the calculation of DMSO concentration

The DMSO percentages given in Table 1 are calculated according to the following method. DMSO has 6H per molecule and its MW is 78 g/mole. This corresponds to 13g DMSO for each H mole. Meanwhile, based on the basic structure of branched GAP (Ref 20), there are 5H per GAP unit with a corresponding MW of 99 which yields an amount of 20g GAP for each H mole. It is assumed that the area integrated under each NMR peak is directly proportional to the H mole number of the corresponding compound. For example, the peak integration for DMSO after the third extraction is 3.80 and the total peak integration for branched GAP is 100. The peak integration of DMSO times 13g DMSO per H mole gives 49.4g DMSO. If the same calculation procedure is applied for branched GAP, it can be deduced that the weight percentage of DMSO in the solution as being 2.4% after the third wash. For these calculations the contributions from -OH groups and -CH- groups at the branching positions of branched GAP molecule were ignored . However, the number of H of those groups is negligible with respect to the total number of H of branched GAP.

2.6 Explanation of the Extraction Method based on Solubility Parameters

The solubility parameter values are most useful for nonpolar solvent mixtures. However, this parameter may help to explain the differential solubility pattern of the whole extraction system. Given that DCM is almost nonpolar and symmetrical, it forms a nonpolar organic phase with branched GAP. Eventhough DMSO is a strongly polar liquid, it can also be completely soluble in a large enough amount of DCM when the latter is added to branched GAP solution. The solubility parameter of DMSO lies in the middle between those of DCM and methanol so that it can be miscible with either DCM or methanol. However, due to a strong polarity of methanol, DMSO, a polar liquid, may preferentially mix with methanol rather than with DCM when the aqueous phase of methanol is added to the mixture. DMSO is thus gradually extracted by the methanol. The water is used to form a distinct aqueous phase for the extraction process. The presence of NaCl salt in brine may help to reduce the foaming phenomenon at the interface of the two liquid phases. Methanol can also extract some branched GAP chains because of the presence of some -OH groups in branched GAP molecules. However, it is expected that only shorter chains of branched GAP can be extracted by methanol since they are supposed to be more polar than the longer chains.

2.7 Nomenclature and Reaction Parameters of Branched GAP Samples

Table 2.1 summarizes the reaction parameters used for the syntheses of the branched GAP samples. The nomenclature of these samples will be referred to in the chapters dealing with the characterizations and mechanical testing.

Table 2.1
Nomenclature and Reaction Parameters of Branched GAP Samples*

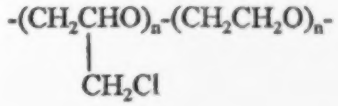
Parameters	DGAP11	DGAP12	DGAP14	DGAP16	DGAP18
PECH (g)	50	50	50	50	50
DMSO (g)	500	500	500	500	500
POLYOL/PECH	0.50(GOL)	0.10(TMP)	0.20(TMP)	0.10(PE)	0.20(PE)
NaN_3 (g)	40	32	32	32	32
CH_3OLi/PECH	0.04	0.03	0.03	0.03	0.03
Reaction time (h)	21	21	7	7	21

* All samples were prepared at a reaction temperature of 120°C

3.0 BRANCHED GAP-ETHYLENE OXIDE COPOLYMER

3.1 Starting Materials

All the reactants used to produce the branched GAP-Ethylene Oxide copolymer, GEC, are exactly the same as for the synthesis of second generation branched GAP except the rubbery polyepichlorohydrin (PECH). The latter has been replaced by the polyepichlorohydrin-ethylene oxide copolymer, namely PEEC with a weight proportion of 68% PECH and 32% EO. The chemical structure of PEEC is represented as follows (Ref 22):



However, the detailed structure as well as the solution properties of this copolymer have not been yet investigated to show if it is amorphous or partly crystalline. This product also comes from BF Goodrich Co. under the trade name Hydrin 200, it is a yellow rubbery solid with an appearance similar to PECH (Hydrin 100).

3.2 Synthesis

Different preliminary methods were tried using varied amounts of solvent, a different reaction time, different temperature, or lowering the temperature before adding NaN_3, etc. The following method ended up being the best one.

The polymerization apparatus is the same as used for the synthesis of branched GAP. It is a cylindrical flask in Pyrex of 7 mm thickness, with a maximum volume capacity of 600 mL and having four openings as described in chapter 2. To the polymerization system, 500g of DMSO was added as well as 50g of comonomer previously cut into small pieces. This reaction flask was placed in an oven at 60C overnight to allow the comonomer to dissolve in DMSO. The following morning, the cap, the stirrer, the condenser and the thermometer were added to the reaction flask and secured with a clamp. The reaction flask was placed in the heating mantle and heated. When the temperature reached about 50-60C the stirrer was turned on. When the temperature reached 120 ± 3°C, TMP or glycerol was added. The system was stirred and the temperature was maintained at 120C for 45-50 minutes. Then, NaN_3 was slowly added to the mixture. Thirty minutes later, CH_3OLi was added. The whole system was kept at 120C and vigorously stirred for at least 7 hours.

3.3 Purification Method

The resulting solution after the period of synthesis of branched GEC was filtered to separate the solid powder of salts (NaCl and unreacted NaN_3). The organic phase was prepared by adding

a two fold volume of DCM to the solution. Then three extraction steps were performed using a mixture of 60% methanol and 40% brine to remove DMSO from branched GEC . The third extraction was allowed to stabilize overnight. About 5g of $MgSO_4$ powder was added to dry the solution of copolymer. The salt was then filtered. The remaining DCM was easily evaporated using a Rotovap over three hours, the first hour at 50°C and then two hours at 80°C. The final step consisted of evaporating the last traces of DMSO as well as water using a vacuum oven at 80°C for a few hours. It is noted that by using a higher composition of methanol in the extracting solution, it might be possible to carry out the extraction process by only three steps the final product having the same purity as that obtained from the four-step method described in Chapter 2. This is also checked by NMR spectra.

Generally, the purification of GEC solutions was slightly more difficult than that of GAP solutions because of a higher degree of foaming between organic and aqueous phases.

3.4 Summary of the Branched GEC Samples

All GEC samples obtained have similar appearance which is dark brown in colour. Their nomenclature as well as reaction parameters are summarized in Table 3.1. This nomenclature will be referred to in the following chapters.

Table 3.1
Nomenclature and Reaction Parameters of Branched GEC Samples

Parameters	DcomA6	DcomA9	Dcom21	Dcom23	Dcom25	Dcom27
PEEC (g)	50	50	50	50	50	50
DMSO (g)	400	510	510	510	510	510
POLYOL/PEEC	0.50 (GOL)	0.50 (GOL)	0.10 (TMP)	0.15 (TMP)	0.10 (PE)	0.30 (PE)
NaN_3 (g)	40	40	40	40	40	40
CH_3OLi/PEEC	0.03	0.04	0.03	0.03	0.03	0.03
Tempera.(°C)	120	120	115	115	115	115
Time (h)	8.5	20	20	20	20	20

4.0 MOLECULAR WEIGHT OF BRANCHED GAP AND GEC SAMPLES

4.1 Gel Permeation Chromatography

The chromatograph used was a Waters, model ALC 200 series, instrument operating at room temperature using HPLC grade THF as a solvent with a flow rate of 1.0 ml. min^{-1}. A multipore ultrastyragel column was used with an effective MW range from 1000 to $1x10^6$. A refractive index detector Shodev SE-51 was used. Data were analyzed using a computer.

The GPC calibration was performed with six polystyrene standards ranging from 4,000 to 600,000 by plotting log MW versus elution volume. The conversion from PS MW to GAP or GEC MW was done as reported in Ref. 20 by combining the hydrodynamic volume ($[\eta]M_w$) concept (Ref. 23) with the Mark-Houwink relation $[\eta] = KM_w^a$

The Mark-Houwink relations reported in literature for Branched GAP (2nd Generation) in THF (Ref. 21) and for Polystyrene in THF (Ref. 24) are respectively:

$$[\eta]_{GAP(2nd\ Generation)} = 2.80 \times 10^{-4} M_w^{0.62} \quad (1)$$

$$[\eta]_{PS} = 9.1 \times 10^{-5} M_w^{0.746} \quad (2)$$

For a given elution volume, both PS and GAP or GEC have the same hydrodynamic volume $[\eta]M_w$; by combining the Mark-Houwink equations (1) and (2) **for branched GAP or GEC and PS** respectively, the following relation was obtained (Ref. 20):

$$M_{GAP} = 0.51\ M_{PS}^{1.075} \quad (3)$$

Therefore, by using eq.(3), the PS calibration curve could easily be transposed to give the calibration curve for branched GAP from which the MW averages for branched GAP or GEC could be computed. The values of M_w and M_n obtained from GPC for Branched GAP and GEC samples are listed in Table 4.1 . Due to the absence of the Mark-Houwink constants, K and a, for branched GEC, eq.(3) was also used for the latter knowing that the presence of ethylene oxide in comonomer may slightly alter the hydrodynamic behaviour of GEC with respect to that of branched GAP.

Table 4.1
MW and Polydispersity of Branched GAP and GEC Samples

Polymer	Sample	M_n GPC	M_w	M_v Viscometry	$(M_w/M_n)_{GPC}$
	Linear GAP(Rockwell)			2,400	
	DGAPA11	11200	19000	18200	1.70
	DGAPA12	12100	20300	18800	1.68
GAP	DGAPA14	13200	21100	22600	1.60
	DGAPA16	12600	25300	22700	2.00
	DGAPA18	14500	27500	28700	1.90
	DcomA6	19500	39200	35300	2.01
	DcomA9	17400	36500	34200	2.10
GEC	Dcom21	24600	47800	45400	1.94
	Dcom23	25400	46200	40500	1.82
	Dcom25	20700	40500	35800	1.96
	Dcom27	21200	37300	34800	1.76

4.2 Solution viscosity

The viscosity measurements of branched GAP and GEC solutions in THF were carried out at 25°C using a modified Ubbelohde viscometer, model 50/104. The Gallenkamp viscometer bath was controlled within ± 0.02°C and the flow times of solutions were measured using a Wescan automatic timer at better than ± 0.01 s.

The intrinsic viscosity, $[\eta]$, obtained from experimental data were used through equation (1) to calculate the viscometric average molecular weight, M_v, of various branched GAP and GEC samples. The results, also presented in Table 4.1, are found to be in good agreement with those deduced from GPC study. The reliability of the obtained viscometric data may also be checked by zcomparing it with the value of the linear GAP (obtained from Rockwell) which is known as being

approximately 2,000. The observed small difference may be attributed to the experimental error and to the different hydrodynamic behaviours of the linear and branched structures of GAP molecules as already mentioned above.

4.3 Discussion

As shown in Table 4.1, most of branched GAP and GEC samples have a polydispersity index, represented by the ratio M_w/M_n, between 1.60 and 2.10. This type of MW distribution may be considered low for polymers resulting from a degradation process.

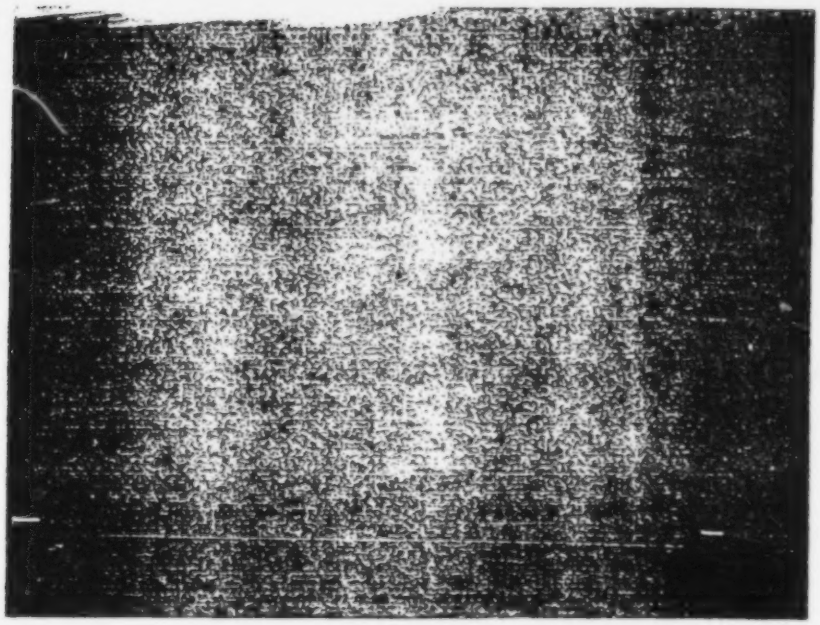
The first GAP sample, DGAPA11, obtained with a high ratio of GOL/PECH (0.50), a moderate ratio of $LiOCH_3$ /PECH (0.04) and a reaction time of 21 hours, appears to have the lowest average MW values. However, these MW values are a little higher than the ones reported in Reference (20) for approximately the same reaction conditions. This could be explained by the fact that rubbery PECH (Hydrin 100) used in this study had a higher MW than the Hydrin (H 45) starting material of Ref. 20. Samples P12 and P14 prepared using TMP with a low ratio Polyol/PECH of 0.10-0.20 and a lower ratio (CH_3OLi/PECH) of 0.03 had approximately the same MW as sample P11. On the other hand, samples P16 and P18 obtained with PE had higher MW and polydispersity than samples P12 and P14 prepared with TMP.

In general, the average MW of GEC samples are larger than those of branched GAP samples. This may be interpreted in two ways: first, the presence of the ethylene oxide groups in PEEC molecules could decrease the extent of degradation during the course of synthesis compared to PECH molecules; secondly, the presence of those groups inside the resulting GEC molecules certainly alter their hydrodynamic behaviour with respect to that of branched GAP molecules so that the Mark-Houwink constants appearing directly in eq.(1) and indirectly in eq.(3) are not accurate enough when applied to the GEC solutions. Since the Mark-Houwink constants for poly(ethylene oxide) in THF solutions are not available, the ones for poly(propylene oxide) in THF solutions found from Ref. 24 could tentatively be used for the former:

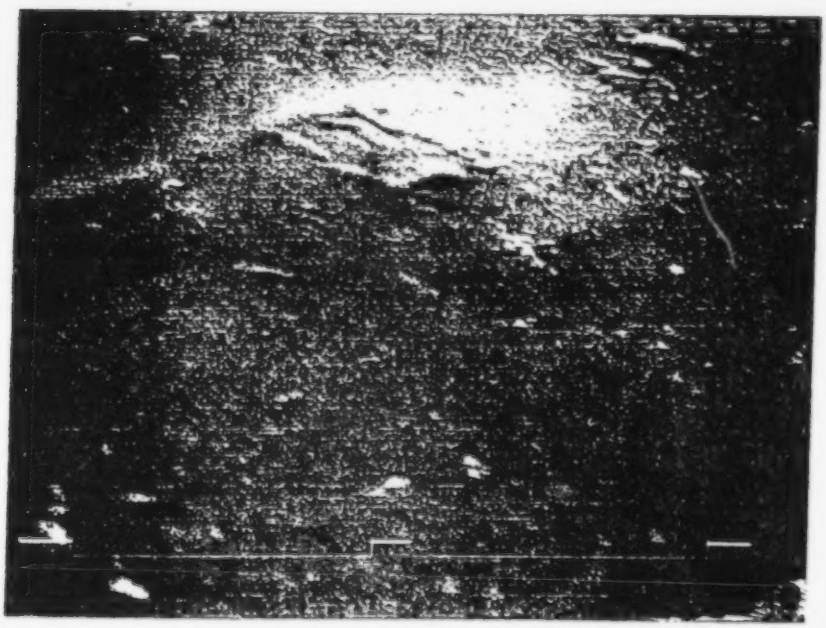
$$[\eta] = 5.5 \times 10^{-4} M_w^{0.62} \qquad (4)$$

By taking into account the composition of PEEC (about 30% in weight of ethylene oxide) and based on eqs. (1) and (4) , it is estimated that the average MW presented in Table 4.1 for GEC samples were over-evaluated by a factor of approximately 15% such that the discrepancies between the average MW of branched GAP and GEC could be advantageously reduced.

(4)



(5)



Figures 4 & 5 - SEM of a Typical Branched GAP Polyurethane:
(4) X1000 ; (5) X5000

5.0 CURING AND TESTING OF ENERGETIC POLYURETHANES

For the purpose of making the most reliable comparison between the performances of the second generation branched GAP and the newly synthesized branched GEC, both of them will be cured by exactly the same procedure with all experimental conditions being identical. After curing, the obtained energetic polyurethane samples will be characterized and mechanically tested by the same methods.

5.1 Curing of Branched GAP and Branched GEC

All the curings of the second generation branched GAP, as well as branched GEC, were performed at 60°C using only Isophorone diisocyanate (IPDI) as the curing agent. The oil bath and the vacuum oven were set and preheated at 60°C prior to curing process. The exact amount of branched GAP or branched GEC was weighed in a 50 ml beaker and then introduced into the vacuum oven where high vacuum was applied for at least 1 h in order to remove traces of impurities such as water, DMSO... Then the beaker was installed in the oil bath before adding the desired quantity of IPDI to satisfy a fixed NCO/OH ratio. The mixture was stirred for about 3 minutes and then transferred into the molds made in teflon according to the ASTM 638 standard for plastic-elastomeric materials. The molds were also preheated to 60°C in order to prevent any temperature fall in the reaction mixtures.

Vacuum was then applied for about 15 minutes in order to remove all air bubbles from the samples. However, due to the high viscosity of the curing media, there were some small voids still hidden inside the cured samples. The molds were kept overnight in the oven at 60°C and then about 1 h at 100°C to complete the curing reaction.

All the NCO/OH ratios were calculated by tentatively taking the hydroxyl equivalent weight of branched GAP and GEC as being 1500 g. For each set of NCO/OH ratio, at least three specimens were produced for the tensile test.

5.2 Morphology of cured samples by SEM

The cured energetic polyurethane samples still contained some small voids resulting from the difficulty in removing all air bubbles from the highly viscous media.

However, all cured samples are completely transparent without any apparent phase segregation observed In order to check this morphology, the scanning electron microscopy (SEM) technique was applied to some samples using a JEOL, Model JSM T100, with a magnification of X1000 and X5000.

Figures 4 and 5 show the morphology of typical energetic polyurethanes from branched GAP. There is no microphase observed through the continuum matrix which means that these samples are perfectly homogeneous after the curing is completed.

5.3 Thermomechanical Analysis (TMA)

In order to determine the glass transition temperature, T_g, of the energetic polyurethanes, the thermomechanical analysis was applied to some typical samples of these polyurethanes. This technique is based on the principle that there is an abrupt change in the coefficient of expansion of the sample when it passes through the softening or glass transition temperature under a constant heating. This manifests itself as a break in the heating curve. The T_g is defined as that temperature at which the regression line before the break, intersects that after the break.

TMA was performed using a Mettler TA-4000 with a TMA 40 measuring cell. The approximate sample dimensions were 3 mm thick in the direction of measurement and 6 mm in diameter. Measurements were carried out in the range of -100 to 50°C. A low-temperature accessory was used with liquid nitrogen as refrigerant. The heating rate was 10°/min and the constant probe force applied to the sample
was 0.02 N.

5.4 Tensile Test

The most significant evaluation of energetic polyurethanes is certainly the tensile test. This was performed on cured samples using an Instron Tester, model 4206, where the force applied to the sample as well as its elongation during the test were automatically recorded by the control board of the tester. The tensile load cell has a capacity of 5 kg or 50 N. A suitable grip for elastomeric materials was used for correctly holding the sample in place without slipping. The crosshead speed used was 10 cm/min. Prior to testing, the width and thickness of the gauge region of each test specimen was measured to an accuracy of ± 0.5 μm using an electronic micrometer. Usually, the gauge dimensions were approximately (25 x 6 x 3) mm. All specimens were drawn at ambient temperature. The mechanical properties of interest are defined as follows (Ref. 25):

Elongation at break (ξ_b) = (Gauge length at break/Initial gauge length) x 100%

Tensile strength (σ_u) = (Ultimate tensile force x ξ_b)/(Original cross-sectional area)

These two quantities were directly produced by the computer using the software provided by Instron Company and they may be checked by the extension and the load recorded on the keyboard control of the Instron system.

5.5 Results and Discussion

5.5.1 Branched GAP Samples

Due to the large amount of the DGAPA13 sample produced, the curing of this sample has been performed covering a large range of the NCO/OH ratio, varying from 0.57 to 2.28, in an attempt to optimize the NCO/OH ratio according to the choosen value of 1500 for the equivalent weight of branched GAP. Only some typical values of the NCO/OH ratio were selected for the curing of the other GAP samples. The mechanical properties as well as the glass transition temperature of the obtained polyurethane products are presented in Table 5.1 (for the DGAPA13 sample) and Table 5.2 (for the others).

Table 5.1
Properties of Polyurethanes from Branched GAP Sample (DGAPA13)

NCO/OH	Elongation (%)	Tensile strength (Mpa)	T_g (°C)
0.57	290	0.060	- 26.0
0.77	290	0.24	- 25.3
1.15	170	0.19	- 23.0
1.18	200	0.34	-------
1.50	230	0.43	- 21.3
1.50	210	0.28	-------
1.65	140	0.39	- 21.0
1.67	120	0.79	-------
2.17	200	0.92	- 12.8
2.28	140	0.78	-------

Table 5.2
Properties of Polyurethanes from Other Branched GAP Samples

Sample	NCO/OH	Elongation (%)	Tensile strength (Mpa)	T_g (°C)
DGAPA11	0.62	230	0.25	- 23.3
	0.79	150	0.49	____
	1.22	105	1.59	- 20.2
DGAPA12	0.40	180	0.38	____
	0.65	160	0.43	- 25.7
	0.78	145	0.26	- 24.6
DGAPA14	0.50	190	0.28	____
	0.72	155	0.34	- 22.2
	0.94	120	0.44	- 19.1
DGAPA16	0.60	120	0.18	- 19.8
	0.83	155	0.36	____

The tensile strength of all tested specimens is relatively high and generally increases with the increasing NCO/OH ratio; unfortunately, the elongation at break is still low. These mechanical properties, in reality, could be much higher than the reported values because of the presence of a certain number of micro-voids formed during the curing period in the gauge-length area of each tested specimen. This certainly could have contributed to an earlier breakup of the specimen, leading to a large positive error in the experimental data. It is hard to attribute a fixed error percentage to each value since the void size varied from one specimen to another. The relative errors could easily reach beyond 50% for some tested specimens. Concerning the T_g data obtained from TMA, they are much more consistent than the mechanical data since the small specimens needed for these analyses were cut from the large area of the tensile test specimens where there were likely no voids present. These data together with those of the mechanical properties confirm the trend of increasing tensile strength and T_g with increasing NCO/OH ratio, while the elongation at break is inversely proportional. Due to the uncertainty of the mechanical testing data, it is hard to draw a firm conclusion about the clear effects of the polyol used (GOL, TMP and PE) and its proportion, as well as those of the cleaving agent proportion, on the mechanical performances of the resulting polyurethanes from branched GAP samples.

5.5.2 Branched GEC Samples

The elongation at break, tensile strength, and T_g of polyurethane products obtained from GEC samples are presented as functions of the NCO/OH ratio in Tables 5.3, 5.4 and 5.5.

Table 5.3
Properties of Polyurethanes from Branched GEC Copolymers (DcomA6 and DcomA9)

Sample	NCO/OH	Elongation (%)	Tens.Strength (Mpa)	T_g (°C)
DcomA6	0.63	285	0.16	- 38.6
	0.81	185	0.21	- 38.0
	0.93	190	0.19	-------
	1.21	100	0.45	- 34.2
DcomA9	0.55	330	0.12	- 39.2
	0.77	315	0.23	-------
	0.96	170	0.34	- 37.0
	1.18	150	0.34	- 32.8

The DcomA9 sample prepared with a relatively long reaction time (20 h) and a high cleaving-agent/PEEC ratio of 0.04 gave rise to polyurethane products of better mechanical properties than sample DcomA6 obtained after 8.5 h with a lower cleaving agent concentration of 0.03. The tensile strength obtained for samples A6 and A9 is considered to be high enough but the elongation at break is still low. This may be attributed to the use of too high a GOL/PEEC ratio (0.50) in the syntheses of both samples.

Table 5.4
Properties of Polyurethanes from Branched GEC Copolymers (Dcom21 and Dcom23)

Sample	NCO/OH	Elongation (%)	Tens.Strength (Mpa)	T_g (°C)
Dcom21	0.52	390	0.088	- 41.5
	0.69	510	0.11	-------
	0.83	455	0.14	- 40.3
	0.94	470	0.22	-- -----
	1.18	450	0.21	- 37.2
Dcom23	0.24	515	0.073	--------
	0.40	500	0.048	- 40.7
	0.62	540	0.13	--------
	0.75	480	0.21	- 39.5
	0.79	450	0.084	--------
	0.92	530	0.1	
	1.03	500	0.10	--------

Table 5.5
Properties of Polyurethanes from Branched GEC Copolymers
(Dcom25 and Dcom27)

Sample	NCO/OH	Elongation (%)	Tens. Strength (Mpa)	T_g (°C)
Dcom25	0.48	445	0.15	------
	0.71	700	0.28	-37.5
	0.79	540	0.37	-- ---
	0.80	400	0.13	------
	0.81	400	0.33	- 38.4
	0.94	330	0.38	------
	0.94	405	0.17	- 38.2
	1.00	250	0.15	------
	1.10	310	0.38	- 36.7
Dcom27	0.46	420	0.23	- 38 4
	0.68	515	0.34	------
	0.87	455	0.40	- 36.4
	1.06	290	0.32	------
	1.24	265	0.29	- 33.8

Compared to the specimens of polyurethanes resulting from the branched GAP samples, the GEC samples yielded cured specimens of better appearance, (ie. there were much fewer bubbles inside the gauge-length area of the tensile specimens) such that their elongation at break and tensile strength data are more reliable.

As shown in Tables 5.3, 5.4 and 5.5, GEC samples yield generally polyurethanes products of higher elongation at break but a little lower tensile strength than the products of Table 5.2 obtained from branched GAP. This is also supported by the lower T_g values of polyurethanes obtained from GEC samples. The presence of ethylene oxide groups (-O-CH_2-CH_2-) in the GEC copolymer causes likely a greater flexibility in the resulting polyurethanes which is responsible for their high values of elongation at break.

Branched GEC Copolymers (Dcom 21, 23, 25 and 27) prepared using TMP and PE as polyols in the synthesis reaction, yielded polyurethanes of higher elongation compared to the products obtained from samples Dcom A6 and A9 prepared with glycerol. This could be explained by the fact that TMP and PE contain respectively 3 and 4 primary alcohol groups compared to glycerol which has only two groups. Based on an approximate value of 1500 g for the equivalent weight of branched GAP and GEC, it is found that the optimal value of NCO/OH ratio, to produce an acceptable tensile strength and a high elongation at break for polyurethane products from either branched GAP or GEC samples, is around 0.70.

6.0 CONCLUSIONS

The synthesis of second generation branched GAP using rubbery PECH (Hydrin 100) as the starting material together with glycerol, TMP or PE as the polyol and CH_3OLi as the cleaving agent produced GAP samples of M_w (19,000 - 28,000). Meanwhile, the preparation of a GAP-Ethylene Oxide copolymer based on the same degradation process but using PEEC (Hydrin 200) as the reactant rubber produced GEC samples with M_w (36,000 - 48,000) slightly higher than branched GAP. The purification method based on three or four-step extraction using a mixture of methanol-brine is an effective one to remove DMSO from GAP or GEC samples. This effectiveness was checked using NMR spectroscopy.

The curing of branched GAP using IPDI yielded polyurethane specimens of relatively low elongation at break and high tensile strength; however, these results could be much better if the cured specimens are completely bubble-free. On the other hand, the products obtained from GEC samples have larger elongations at break and acceptable tensile strengths. This may be attributed firstly to a better quality of cured specimens which contain fewer bubbles and secondly to the presence of the ethylene oxide groups in the GEC molecules which give them a higher flexibility.

Polyurethanes based on GEC samples had lower T_g than those obtained from Branched GAP. The polyol reactant used in the synthesis of GEC had an effect on the mechanical properties of the polyurethanes obtained from the copolymers. GEC samples synthesized with TMP and PE yielded products with higher elongation at break compared to those obtained from the copolymers prepared with glycerol.

ACKNOWLEGEMENTS

The authors wish to thank the Defense Research Establishment at Valcartier (DREV) for granting a research contract to carry out this project at the Royal Military College, Kingston, Ontario.

They are also thankful to Mr. R. Whitehead, J. Perrault and J. Irving for their technical assistance.

REFERENCES

1. Frankel, M.B. and Flanagan, J.E., "Energetic Hydroxy-Terminated Azido-Polymer",
- U.S. Pat. 4,268,450, 19 May 1981
- Can. Pat. 1,140,296, 25 Jan 1983.

2. Frankel, M.B., Witucki, E.F. and Woolery, D.O., "Aqueous Process for the Quantitative Conversion of Polyepichlorohydrin to Glycidyl Azide Polymer", U.S. Pat. 4,379,894, 12 April 1983.

3. Earl, R.A., "Use of Polymeric Ethylene Oxides in the Preparation of Glycidyl Azide Polymer", U.S. Pat. 4,486,351, 4 December 1984.

4. Wagner, R.I., Grant, L.R., Wilson, E.R. and Flanagan, J.E., "Glycidyl Azide Polymer and Method of Preparation", Europ. Pat. EP-A-0,380,750, 08 Aug 90.

5. Frankel, M.B., Grant, L.R. and Flanagan, J.E., "Historical Development of GAP", J. Propulsion & Power, Vol. 8, No. 3, p. 560-563, May-June 92.

6. Ahad, E., "Direct Conversion of Epichlorohydrin to Glycidyl Azide Polymer",
- Can. Pat. 1,262,918, 14 November 1989
- U.S. Pat. 4,891,438, 2 Jan 90.

7. Ahad, E., "Process for the Preparation of Alkyl Azide-Substituted Hydroxy-Terminated Polyethers", Europ. Pat. EP- 0,274,213 B1; DE, FR, GB, SE; 13 May 92.

8. Ahad. E., "Preparation of GAP in a one-step Process", Proceedings of the 13th Meeting of TTCP (W4) held in USA, Sept 87.

9. Ahad, E., "Single-Step Synthesis of Glycidyl Azide Polymer", DREV R-4544/89, March 1989, UNCLASSIFIED.

10. Ahad, E., "Branched Hydroxy-Terminated Aliphatic Polyethers",
- Can. Pat. 1,300,171, 05 May 92
- U.S. Pat. 4,882,395, 21 Nov 89
- Europ. Pat. EP-A-0,350,226, 10 Jan 90.

11. Ahad, E., "Branched GAP", Proceedings of the 15th Meeting TTCP (W4), 22-26 Jan 90, DREV, Canada.

12. Ahad, E., "Branched Hydroxy-Terminated Azido Polymers", Proceedings of the 21th International Annual Conference of ICT, "Technology of Polymer Compounds and Energetic Materials", 03-06 July 90, Karlsruhe, Germany.

13. Ahad, E., "Synthesis and Characterization of Branched Glycidyl Azide Polymer", DREV R-4634/91, May 1991, UNCLASSIFIED.

14. Bui, V.T., Rhéaume, D. and Ahad, E., "Polyurethanes Based on Different Glycidyl Azide Polymers", Proceedings of the 15th Meeting TTCP (W4), 22-26 Jan 90, DREV, Canada.

15. Bui, V.T. and Rhéaume, D., "Characterization of Compositions Based on Glycidyl Azide Polymer (GAP)", RMCC/DCCE/FR-91/11, DREV Task 14/1-1988 (Scientific Authority: E. Ahad), Final Report, Nov 91.

16. Villeneuve, S. and Carignan, P., "Binders for Rocket Propellant Formulations Based on Glycidyl Azide Polymers", DREV R-4631/91, Fev 1991, UNCLASSIFIED.

17. Ahad, E., "Branched Energetic Polyether Elastomers",
- U.S. Pat. 5,130,381, 14 July 92
- U.S. Pat. 5,191,034, 02 Mar 93
- Can. Pat. Appl. 2,061,744-6, filed 24 Feb 92
- PCT International Appl. No. PCT/CA92/00144, Filed 03 April 92
- Europ. Pat. Appl. No. 92907672-7, DE, FR, GB, NL, 03 April 92

18. Ahad, E., "Improved Branched Energetic Azido Polymers",
- U.S. Pat. Appl. 08/130,129, filed 04 Oct 93
- Can. Pat. Appl. 2133507, filed 03 Oct 94
- Europ. Pat. Appl. 94307164.7, filed 30 Sept 94.

19. Ahad, E., "A Novel Degradation Process for the Synthesis of Branched GAP", Proceedings of the 18th Meeting TTCP (W4), Fort Halstead, UK, April 93.

20. Ahad, E., "Improved Process for the Synthesis of Second Generation Branched GAP", DREV-R-9414, April 95.

21. Ahad, E., "Characteristics of Second Generation Branched GAP", DREV-R9512/95.

22. Mark, H.F., Bikales, N.M., Overberger, C.G., Menges, G. and Kroschwitz, J.I., "Encyclopedia of Polymer Science and Engineering", Vol. 6, p. 307, 2nd Ed., 1986, Wiley , NY.

23. Grubisic, Z., Rempp, P. and Benoit, H., J. Polym. Sci. (Part B), Vol. 5, p. 753, 1967.

24. Brandrup, J. and Immergut, E.H., "Polymer Handbook", Wiley- Interscience, New York, 3rd Ed., 1989.

25. Peacock, A.J. and Mandelkern, L., J. Polym. Sci., Part B, **28**, p. 1917, 1980.

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TITLE:(U) BRANCHED GLYCIDYL AZIDE COPOLYMERS

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ABSTRACT: (U) Second generation branched Glycidyl Azide Polymer (GAP) and branched Glycidyl Azide-Ethylene Oxide Copolymer (GEC) are synthesized at 120C according to the degradation process developed at DREV using polyepichlorohydrin (PECH) and polyepichlorohydrin-ethylene oxide copolymer (PEEC), respectively, as starting materials, under exactly the same experimental conditions. The main reaction parameters to be varied are: the type of polyol; either glycerol (GOL), trimethyol propane (TMP) or pentaerythritol (PE), as well as its proportion; the cleaving agent concentration; the reaction time and temperature. The average molecular weights (MW) of branched GAP and GEC are measured by the Gel Permeation Chromatography (GPC) and viscometry techniques. In general, GEC has MW values slightly higher than the corresponding branched GAP. Both products are then cured with isophorone diisocyanate (IPDI) at different values of the NCO/OH ratio. The obtained energetic polyurethanes are characterized using Scanning Electron Microscopy (SEM), Thermomechanical Analysis (TMA) and tensile tests. It is found that GEC yielded polyurethane products having higher elongations at break but lower tensile strengths than their branched GAP counterparts.

DESCRIPTORS: (U) Binders (materials);Copolymers;Mechanical properties;Experimentation;Solid rocket propellants;Degradation;Synthesis;Organic azides
IDENTIFIERS: (U) GAP (glycidyl azide polymer) propellants;GEC (glycidyl azide-ethylene copolymer)

REPORT NUMBER: DREV-CR-856; Final Report | **REPORT DATE:** 01 Oct 1995 | **NUMBER OF PAGES :** 38

DRDKIM N°: 96-00416 | **CANDIS N°:** 154752 | **Format(s):**Document Image stored on Optical Disk;Hardcopy

Date modified: 2003-04-17

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